Accelerated Aging Versus Realistic Aging in Aerospace Composite Materials. II. Chemistry of Thermal Aging in a Structural Composite

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ABSTRACT: Samples of an aerospace structural epoxy composite (8552/IM7) were subject to long-term ($\approx$ 1 year) thermal aging at temperatures of 70°, 120°, 170°, and 200°C (in air). The changes to the chemical and physicochemical structure of the composite were analyzed by a range of different techniques, including gravimetric analysis, Fourier transform infrared (FTIR), and dynamic mechanical analysis (DMA) to compare the effects of different severities of degradation treatment. The results highlighted the large differences in chemical effects between the surface and the interior of the composite with very minor changes in the latter even at quite high aging temperatures and long aging times. The oxidative changes at the surface, however, varied from highly selective molecular changes for particular chemical groups at the lower aging temperatures (70° and 120°C), to quite general and extensive oxidative degradation at the higher aging temperatures (170° and 200°C). The results indicated that the mechanical changes in an aged composite of this type will vary greatly with the material thickness and surface protection as well as the aging temperature the composite is exposed to. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3221–3232, 2006

Key words: composite degradation; aerospace epoxy; thermal aging; chemical analysis; gravimetric; FTIR; DMA

INTRODUCTION

The present work is the second in a series[1] detailing the results from an extensive work program that was undertaken to try to develop low-cost, accelerated aging tests for aerospace composites that could be used to replace some of the expensive and time-consuming mechanical testing protocols now required.[2,3] The study was also designed to determine which type of accelerated aging regime would produce a chemical degradation mechanism most similar to those seen in the commercial, "in use" conditions.

In the previously reported work, the composite material studied was a commercial repair epoxy composite, and it was used in a partially cured form. The aging mechanisms were therefore dominated by the effects of the unreacted resin components present in the laminate. The current study involves determining the degradation chemistry of a fully cured epoxy resin in a standard structural aerospace composite (8552/IM7).[4] This and closely related materials have been extensively studied previously in an effort to determine the mechanical effect of accelerated thermal aging treatments;[5–7] detailed information has been obtained of the various physical failure mechanisms under different aging regimes. It is well known that the thermo-oxidative mechanisms of composite aging are very surface selective, whereas many of the commonly used physical testing methods are not.[8] Many studies of the basic chemistry of simplified academic formulations (and model compounds) related to the major aerospace epoxy matrix resin systems have been carried out, and these have shown that amide and acid groups are initially formed by the resin breakdown.[9–18] Much of this work has relied on Fourier transform infrared spectroscopy (FTIR) to determine the chemical changes in these materials. However, it has not generally been possible to conduct similar studies on commercially fabricated, carbon fiber composite samples because of the interference of the fiber and the multicomponent nature of such materials.

The present work reports and compares the different chemical changes and physicochemical effects observed for 8552/IM7 carbon fiber composite subjected to thermal-only aging for up to 7500 h in air at four different temperatures (70°, 120°, 170°, and 200°C). Unidirectional laminate material was used for aerospace qualification reasons. However, one

would expect more extensive chemical changes in woven cloth laminates due to the higher resin levels and lower surface protection from the carbon fiber layers. A subsequent article will report the aging effects on this material at 70°C under conditions of high, medium and low humidity, as well as thermal-spiking experiments on the moisture-equilibrated samples, and the results obtained will be compared to those of the thermally aged 8552/IM7.

8552/IM7 Chemical structure

The 8552/IM7 system has been described by previous workers[6,9] as consisting of an epoxy matrix of both tetraglycidyldiaminodiphenylmethane (TGDDM) and a triglycidylparaaminophenol (TGAP) cured by a mixture of 3,3' and 4,4'-diaminodiphenyl sulfone. A very idealized structure of the matrix would be as shown in Figure 1 but due to crosslink-density considerations in such highly functional monomers, not all the functional groups can react, even at full cure, with the correct stoichiometry. Commercial formulations are unlikely to meet either of these criteria and it is also well known[10,11] that the commercial grades of the epoxy monomers used are far from defect free. This is especially the case with TGDDM.[12] The 8552/IM7 is also believed to contain a toughening agent,[5] which may be a polysulfone thermoplastic. Such a polymer is relatively oxidation resistant and may not contribute to the degradation of the composite at relatively low aging temperatures.

The chemical changes in the aging composite samples were followed by a great range of different techniques, as described in the previous article.[1] However, only the results from the chemically more informative techniques are considered in the present study. These techniques include Fourier transform infrared (FTIR) spectroscopy, gravimetric analysis, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA).
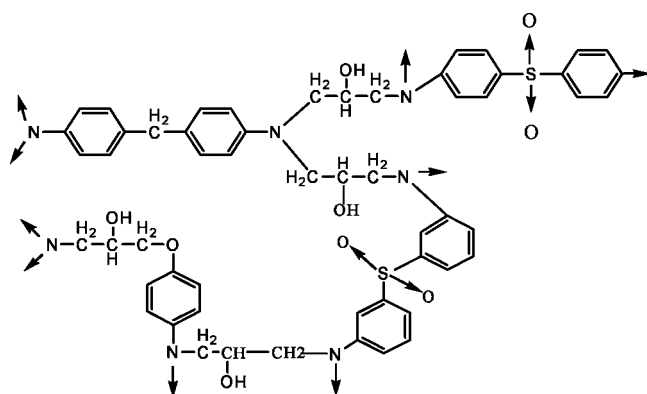

**Figure 1** Idealized chemical structure of 8552 resin.

EXPERIMENTAL

The material selected, 8552/IM7 carbon/epoxy pre-preg,[4] was from Hexcel Composites (Duxford, UK). It was laid up by hand to give a unidirectional laminate with the approximate dimensions of 700 mm × 1000 mm and a 2-mm thickness, and it was cured according to the aerospace standard operating procedures for structural panels (details under commercial confidence). The cured laminates were C-scanned and measured for thickness (consolidation) to ensure the quality of the laminate. The laminate was cut into a series of 50-mm × 50-mm plaques and these plaques were used in all accelerated aging experiments. All plaques were dried at 50°C over phosphorous pentoxide (P_2O_5) until a constant weight was achieved, before aging.

The plaques were aged under four isothermal conditions: 70°, 120°, 170°, and 200°C. The lowest aging temperature of 70°C was set to be representative of a typical temperature that an aircraft surface could reach on the ground due to solar heating. Temperatures were chosen thereafter to aid in the definition of accelerated aging conditions with the upper temperature of 200°C chosen as a limit on the temperature performance of the material and just above the initial glass transition temperature (Tg).

All ovens were temperature calibrated and an isothermal volume of operation defined. The oven at 70°C had P_2O_5 placed in the bottom to minimize the relative humidity. Samples were weighed at regular intervals (≈ 50 h) and witness plaques were removed after 400, 900, 2025, 3600, 5800, and 7500 hours for analysis. Plaques were weighed on a Met-tler Toledo AB 204-S four-decimal-place balance. At least three plaques at each aging temperature were removed from the oven, transferred to a desiccator containing silicate, and allowed to cool to room temperature before being weighed. The laminates were then placed back in the oven and used in the collection of the next data point. The weighing process was optimized to take < 30 min.

DMA was conducted on a Rheometrics Scientific IIIe. This instrument was completely computer controlled and the proprietary software used is known as an Orchestrator. All samples were run on a large frame in dual cantilever mode. The sample was cut in a jig, with a diamond blade saw, to give a reproducible sample width of ∼ 10 mm. The cut was made so that the fiber direction ran parallel with the clamps (i.e., the test was conducted in the least stiff direction, facilitating investigation of the resin properties). A multifrequency analysis was undertaken at 1, 10, 50, and 100 Hz, over a temperature range of 25–350°C, at a heating rate of 5°C min^{-1}. Glass transition temperatures were derived from the onset of the decline in the loss modulus (E'_{onset}) and by the tan δ peak position at 1 Hz.
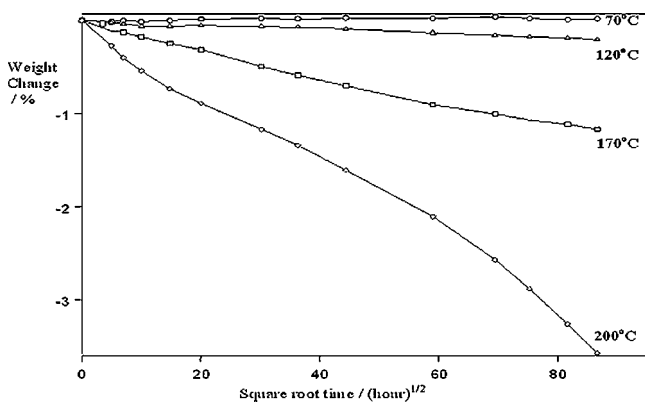
Figure 2 Percentage mass change of the 8552/IM7 matrix as a function of the square root of time (hours[1/2]) at all temperatures over the 7500 h.

All DSC analyses were conducted on a Mettler Toledo 821 with Star Software version 6. Samples were run in alternating DSC mode with an underlying heating rate of 5°C min^{-1}. Samples were encapsulated in lightweight aluminum pans (13 mg). A sample size of 10–30 mg was used. Percentage residual cure was determined by measurement of the enthalpy associated with the unreacted resin and compared with the enthalpy from prepreg for a similar dynamic scan.

To obtain a FTIR, ~ 1.5 mg of previously dried composite was cut from the surface of the aged laminate. This was ground up with ~ 50 mg of anhydrous KBr and subsequently pressed into a disc. The disc was analyzed in a Perkin-Elmer 2000 FTIR spectrophotometer, in transmission mode using KBr as the background reference. Analysis was undertaken by direct comparison of original spectra and by computer-enhanced difference spectra.

RESULTS

Gravimetric analysis

The weight-change measurements carried out during the aging tests were performed on relatively large (50 mm × 50 mm × 2 mm) composite plaques containing high levels of carbon fiber, but the chemical changes, and hence the real weight changes on the dried samples, were almost entirely due to the resin matrix, which is only about one-third the material bulk. Also, in these simple thermo-oxidative aging experiments, the main chemical changes occurred from the surface inward and generally did not penetrate very far, except at the higher aging temperatures and longer aging times. This meant that even quite low percentage weight changes in the plaques equate to very significant chemical changes at the composite surface.

Figure 2 displays the percentage mass change of the 8552/IM7 matrix as a function of the square root

of time (hours[1/2]) at all temperatures over the 7500 h of the experiment. If only one mechanism of degradation were involved the data obtained would have give straight lines, but this is not the case. At the higher temperatures (170° and 200°C) weight loss started immediately. Both traces show evidence of a slowing degradation rate at an intermediate stage, but toward the longer aging times the 200°C trace also shows an accelerated weight change again; indicating a number of mechanism changes are involved during the aging process. Even at the 200°C aging temperature, the total weight loss was only 3.57% after 7500 h, but the chemical analyses (displayed later) show that the resin surface was almost completely degraded.

Figure 3 displays a highly expanded version of the weight loss curves over the range of aging temperature and it gives an indication of a slight (but experimentally significant) oxidative weight increases at 70°C with a number of mechanism changes evident in the 120°C trace. Even though these changes are smaller than those seen in the previous work with the repair epoxy,[1] they are also most likely attributable to the effects of small amounts of defect structures in the composite.

Thermogravimetric analysis (TGA)

While TGA analyses at a range of programmed temperatures were carried out the results obtained were inconsistent. This is a common effect in the TGA of composites because of the difficulty in obtaining a reproducible sample size containing a consistent amount of ground resin with a consistent amount of fiber.

Thermal analysis

Differential scanning calorimetry

The DSC experiment measures the exothermic energy of any residual reactions present in a composite mate-
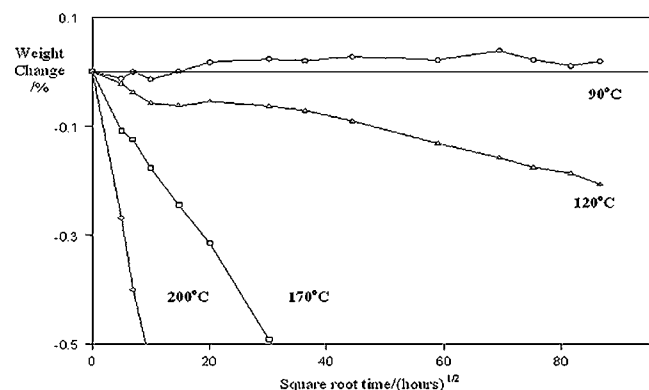
Figure 3 Plot of weight change against square root of time for 8552/IM7 matrix; expansion of weight changes at ~ 0%.
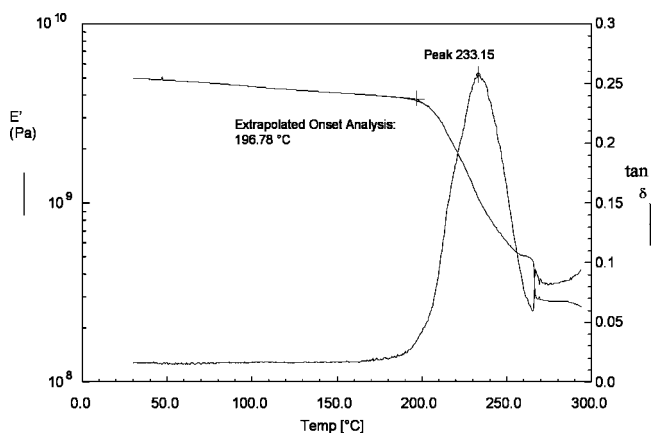
Figure 4 DMA trace for un-aged 8552/IM7.

rial as the temperature increases at a relatively rapid rate (10°C/min in these experiments). The aerospace industry uses this measure of residual exothermic energy (below an arbitrary cut-off temperature) as the remaining cure percentage of the composite. For the commercially manufactured 8552/IM7 composite, the percentage "cure" of the as supplied sample was estimated to be above 97%, and aging at all temperatures at 120°C or above showed small but significant increases to the fully cured mark of 100%. However, this technique was not very useful in adding to the understanding of the aging changes in this particular material.

Dynamic Mechanical Analysis

The DMA of a composite material can provide a detailed picture of variations in matrix-resin motions and hence chemical/mechanical changes in the material over a large temperature range. The aerospace industry is particularly interested in the temperature at which the loss of modulus starts (Tg, E' onset) and the shape and position of the tan δ peak. However, it is important to realize that DMA (as with most mechanical testing methods) measures an average result over a relatively thick sample and, as pointed out above for the gravimetric analysis, chemical changes in the composite occur very selectively from the surface.

Figure 4 shows the shape of the DMA trace for the un-aged 8552/IM7 sample. While there are some increases in Tg onset (4 to 8%, at 170–200°C) and tan δ (Fig. 5) on aging as well as small changes in the DMA curve shape, these are not particularly significant as far as aging effects are concerned. The main indication is that at 170°C there is a very quick completion of the residual cure, with little mechanical change occurring thereafter.

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy has been used extensively to study the thermal and photochemical oxidation of neat

epoxy resin systems over many years.[10,13–18] Many of these systems have been aerospace-type formulations related to the 8552/IM7 material (although generally highly simplified) and a very good library of peak positions for each molecular structure has been built up. Table I is a modification of the table produced by Musto et al.[19] with additions made to help emphasize the differences between the 3,3′ and 4,4′ DDS spectra, as described in earlier work.[9] While the FTIR spectra of epoxy/carbon composites are more difficult to obtain than neat resin spectra, the carbon does not appear to interfere significantly, and equally good spectra of new and aged materials can be obtained, as seen for the un-aged 8552/IM7 composite (Fig. 6). A great advantage of the FTIR work is that only small amounts of material (1–2 mg) are required and therefore a number of samples can be obtained from one specimen at different areas and depths with little noticeable specimen damage.

To compare the FTIR spectral changes in a polymer or composite material during the aging process, it is desirable to use an unchanging spectral peak for normalization purposes (or by the use of differential spectra, as shown in Ref. 19). In this study, for spectral comparison purposes, normalization was carried out using two separate peaks each in different spectral regions. While the aging changes in the current (fully cured) epoxy are not as dramatic as seen in our previous report,[1] the least variable peak at < 2000 cm^{-1} appears to be the 1149-cm^{-1} (probably —SO$_2$-) and not the commonly used 1511-cm^{-1} (aromatic) peak. Above 2000 cm^{-1}, the peaks for aromatic CH in the 3060-cm^{-1} region appear to be the only relatively constant peak for most of the aging temperature range.

Differential spectroscopy has also been a useful technique for highlighting small changes in the spectra with time. Great care had to be taken to duplicate
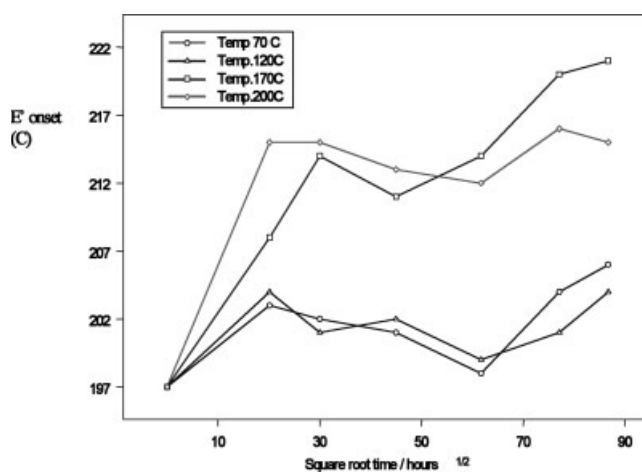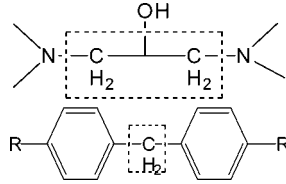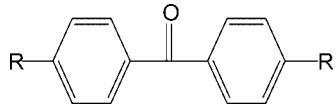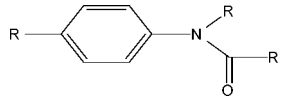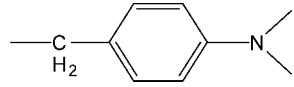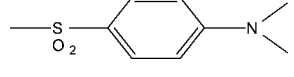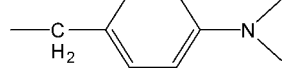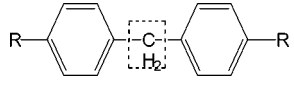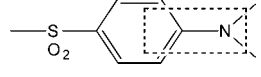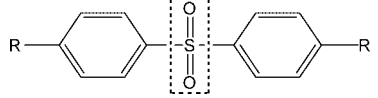

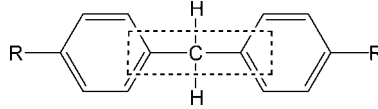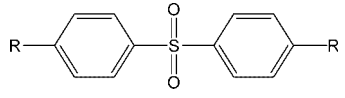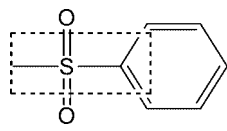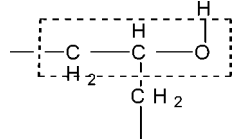**Figure 5** Tg (E'_{onset}) as a function of time and temperature for isothermally aged 8552/IM7.

Approximate peak position (cm^{-1})	Tentative assignment	Functional group
3600–3550	Water	H_2O
3600–3380	ν(O—H); hydrogen bonded	R—O—H······
3380–3200	ν(N—H)	R—N—H
3028–3006	ν(Ar—H)	
2980–2780	ν(C—H) and ν(CH$_2$) TGDDM, DDS	
1725	ν(C=O) aldehyde or ketone	
1710	ν(C=O) aliphatic carboxylic acid	
1695	ν(C=O) aromatic carboxylic acid	
1685	ν(C=O) ketone	
1667	ν(C=O) amide	
1611	Ring quadrant stretching I, TGDDM	
1594	Ring quadrant stretching I, DDS	
1514	Ring semi-circle stretching I, TGDDM	
1453	ν (CH$_2$) TGDDM	
1359–1341	ν(Ar—N), TGDDM, DDS	
1289	ν_{as}(SO$_2$)	
1232, 1188	ν(Ar—C—Ar)	
1150	ν_s(SO$_2$)	
1105	ν(Ar—S)	
1075	ν(C—C—O), secondary alcohol	

*From Musto et al.[19]
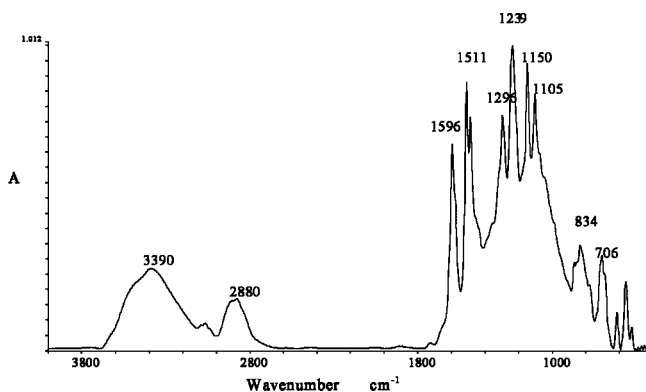
Figure 6 Mid-FTIR surface analysis of un-aged 8552/IM7.

Figure 8 Differential spectrum of 8552-IM7 aged at 70°C for 7500 h and the un-aged sample.

the specimen storage and spectral analytical techniques, so that the method would average out any of the unchanged peaks.[19] The spectrum shown in Figure 6 is of a well-dried starting composite and confirms that the structure contains both TGDDM and TGAP epoxy resins and that it is cured by a 4,4' and 3,3' DDS mixture.[9] However, no attempt was made to find peaks definitely attributable to the polysulfone toughener alone or other possible commercial additives.

Thermal aging changes, 70°C

While spectra were taken at regular intervals (7 times over 7500 h) at 70°C both at the surface and in the center of the laminate, the changes were quite small even after 7500 h. However, the high consistency of the spectra indicated that these changes were real. Figure 7 shows the main changes occur in the OH/NH region of 3500–3300 cm^{-1} (slight increase and then a significant decrease), the CH$_2$ region of 3000 cm^{-1} (decrease), the carboxyl area at

1718 cm^{-1} (increase), and the double bond/aromatic area of 1640–1600 cm^{-1} (decrease). The last spectrum (at 7500 h) showed the first indication of the formation of an amide peak at ≈ 1660 cm^{-1}.

The differential spectrum (Fig. 8) confirms these changes and indicates further sharp changes at ∼ 1600 cm^{-1} as part of the peak moves from 1595 to 1580 cm^{-1} and a decrease occurs in the 1511 cm^{-1} peak. While both of these peaks are due to aromatic CH vibrations (Table I) and hence the overall absorption should not be decreased by such mild aging conditions, their exact peak positions are affected by changes in the attached aliphatic structures.[9]

The center spectral changes are even less than those seen on the surface and can only be evaluated by differential spectra. While the aromatic peaks behave as they do for the surface spectra, it appears that the OH/NH peaks and the carboxyl peaks do the opposite, i.e., they increase ∼ 3400 cm^{-1} and decrease at 1720 cm^{-1} on aging for 7500 h at 70°C.

Although all the spectral changes at 70°C are small they are highly significant because this is the most realistic temperature for long-term "in service" conditions seen by military aircraft. These chemical changes are similar to those seen on a chemically related aerospace composite after 10 years environmental aging[20,21] and contrast to the changes seen in the accelerated aging conditions below.
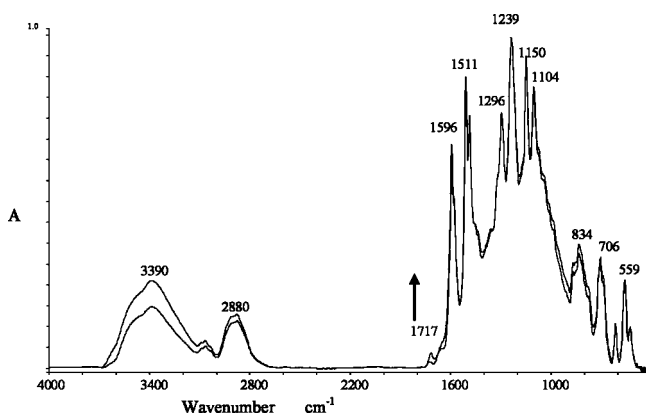

Figure 7 Mid FTIR surface spectrum of un-aged 8552/IM7 and isothermally aged 8552/IM7 at 70°C for 7500 h (and the observed changes with aging time).
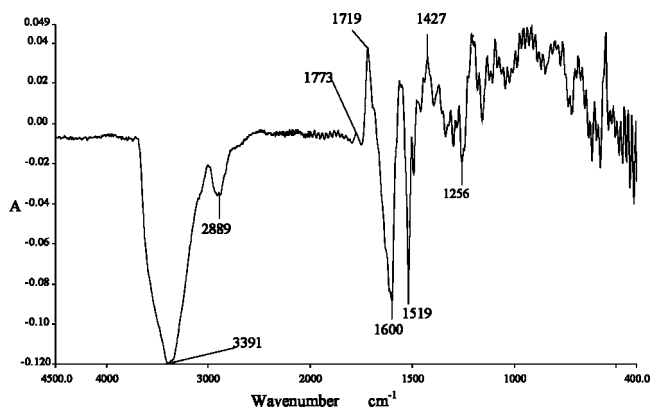
Thermal aging changes, 120°C

The spectral changes seen at the 120°C aging temperature are much greater and considerably different from those seen at 70°C, as expected. Many of these are similar to those described by previous workers who have studied the oxidative degradation of neat resin samples from much simpler epoxy formulations.[13–18] The most noticeable change is the steady and strong formation of an amide peak at 1668 cm^{-1}
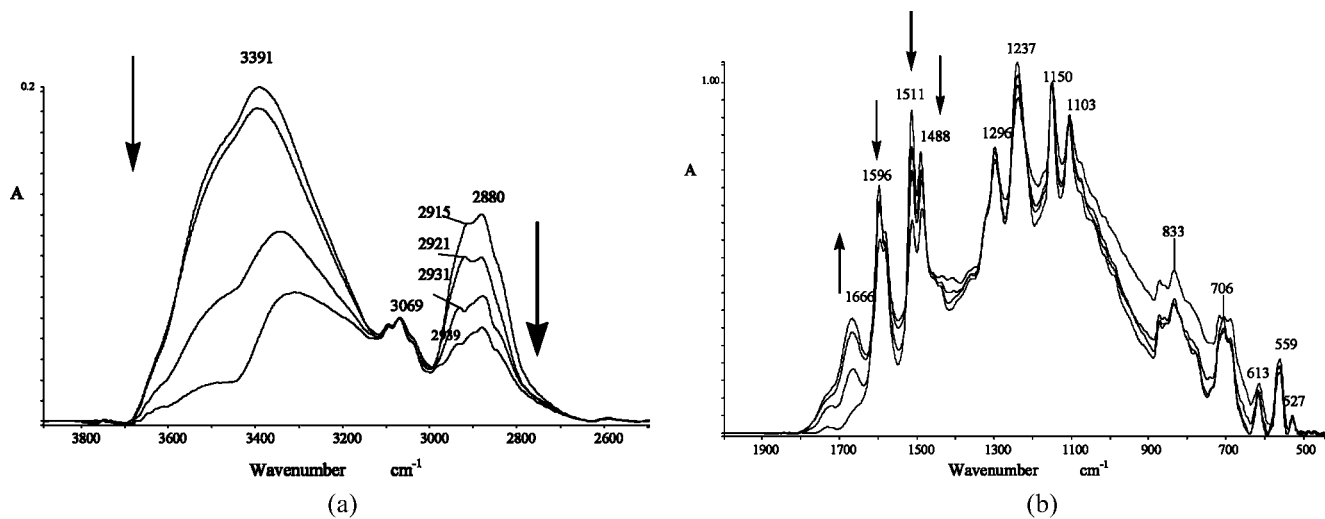
Figure 9 (a) Expanded region (3900–2700 cm^{-1}) of the mid-FTIR surface spectra of 8552/IM7 aged at 120°C over 7500 h. Arrows indicate the decreases in spectral intensity observed with increasing aging time from time zero to 2025, 5800, and 7500 h at 120°C. (b) Expanded region (2000–550 cm^{-1}) of the mid-FTIR surface spectra of 8552/IM7 aged at 120°C over 7500 h. Some spectral changes observed with increasing aging time from time zero to 900, 5800, and 7500 h at 120°C are shown.

accompanied by the smaller carbonyl absorptions at ~ 1720 cm^{-1} [Fig. 9(a,b)].

The amide peak in particular is quite sharp at this temperature indicating that there is probably only one type of structure being oxidized. The carbonyl peak formation (which was the major change at 70°C) starts to increase quite strongly but quickly levels out (at ~ 4000 h) as a slightly lower wavelength (≈ 1715 cm^{-1}) carbonyl forms; indicating the complete oxidation of one (defect?) structure and the start of a different mechanism of oxidation. The other very noticeable changes include the large loss of OH peaks above 3400 cm^{-1} and a smaller drop in the NH absorptions in the 3300-cm^{-1} region. Similarly a steady (but variable with wavelength) drop is seen in the various CH$_2$ absorptions at ~ 2900 cm^{-1}. What is much less noticeable, but very evident in difference spectra (Fig. 10), are the changes in the 1600- and 1500-cm^{-1} regions as major aromatic peaks shifted from 1595 to 1580 cm^{-1} and 1511 to 1486 cm^{-1} (as found with the 70°C aged specimen to a much smaller degree). Minor changes are also noted in the 850- and 700-cm^{-1} region due to similar aromatic peak changes. Again it was a question of peak shifts rather than peak losses at these temperatures, so these differences observed are probably caused by changes in adjacent aliphatic groups, and not losses of aromatic structures as suggested by some previous workers.[15,17]

The center mid-FTIR spectral changes at 120°C are also very small and only significant in the differential spectra, with the minor shift changes in the major aromatic peaks (1595 and 1511 cm^{-1}), which shifted in the surface sample spectra. At the center

of the sample there was no indication of significant oxidative loss of hydroxyls to form carbonyl or amide groups.

Thermal aging changes, 170°C

Even during the early stages of the 170°C aging environment exposures, it was evident that the chemical changes in the matrix resin were considerably different from those seen in the lower-temperature environments. The oxidation product peaks between 1800 and 1640 cm^{-1} were very broad [Fig. 11(a)] even at 400 h, indicating a large mixture of products was being formed rather than largely one type of amide structure which was seen at 120°C. This area continues to increases during the aging treatment, and while amide structures at ~ 1670 cm^{-1}
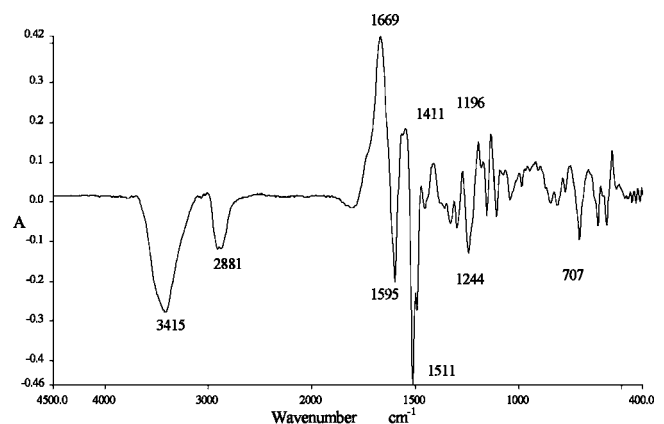
Figure 10 Differential spectrum of 8552/IM7 aged at 120°C over 7500 h and time zero.
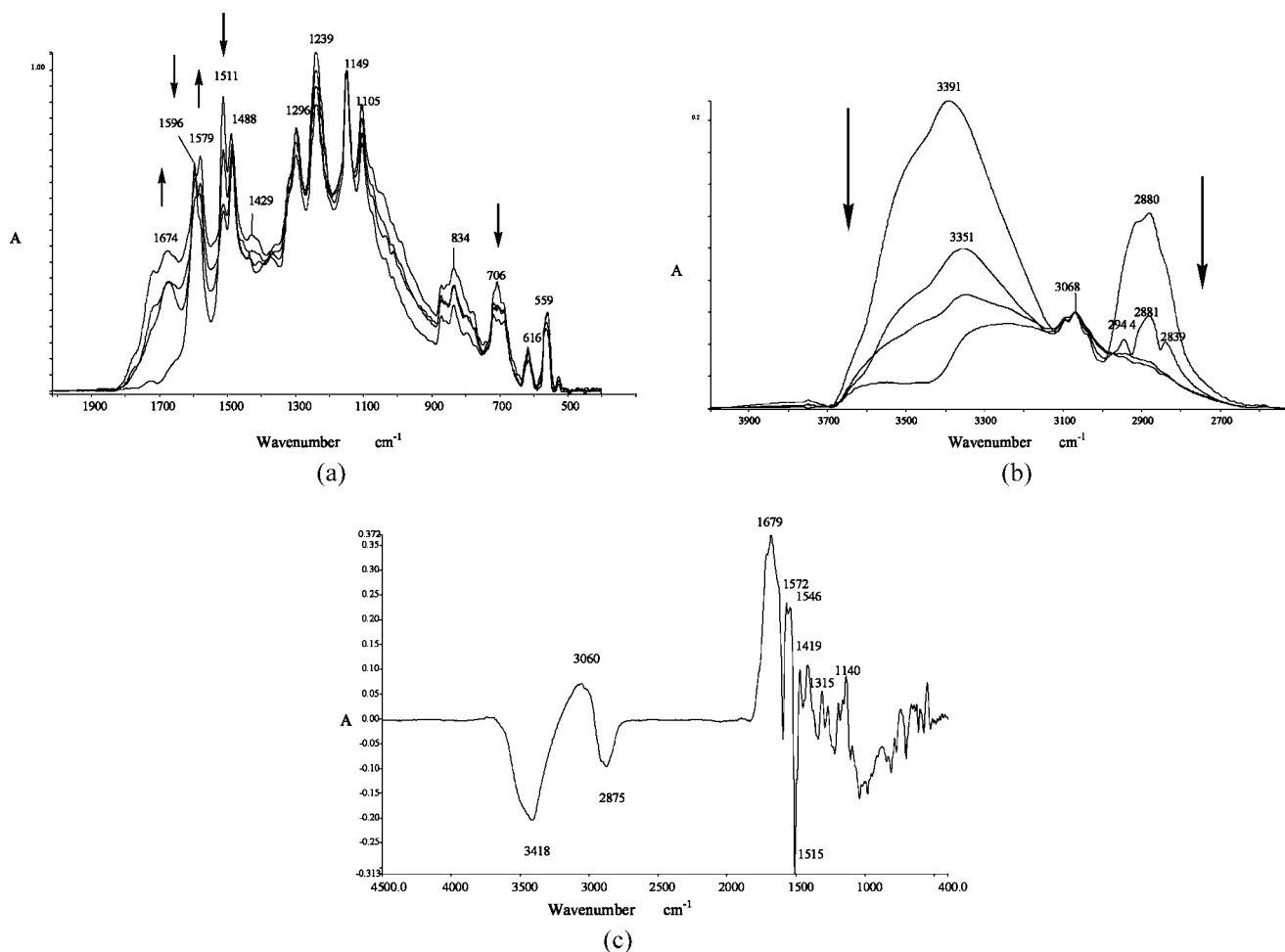
Figure 11 (a) Expanded region of the mid-FTIR surface spectra of 8552/IM7 aged at 170°C over 7500 h. Some spectral changes observed with increased aging time from time zero to 400 and 7500 h at 170°C are shown. (b) Expanded region of the mid-FTIR surface spectra of 8552/IM7 aged at 170°C over 7500 h. Some spectral changes observed during increased aging time from time zero to 400, 3600, and 7500 h at 170°C are also shown. (c) Differential spectrum of the surface of 8552/IM7 after aging at 7500 h at 170°C (subtracted from the un-aged 8552/IM7).

were still present, they were obviously more complex. This area probably includes a conjugated ketone formation ($\approx$ 1680 cm^{-1}) such as that caused by the oxidation of the central —CH$_2$ in TGDDM, as suggested by previous workers.[22] The strong increase in carbonyl absorption between 1715 and 1700 cm^{-1} indicated the formation of acidic products formed by extensive oxidation of aliphatic structures. These changes coincide with the drop in OH areas ($\approx$ 3500 cm^{-1}) and a sharp drop in the CH$_2$ peaks ($\approx$ 2900 cm^{-1}) [Fig. 11(b)]. The changes to the aromatic peaks at 1595 and 1511 cm^{-1} were similar in type to those seen at 120°C (at very much longer times) although the 1511-cm^{-1} peak showed mainly loss with little switch over to 1485 cm^{-1}, in contrast to the 1595-cm^{-1}/1580-cm^{-1} change. It appears that a much more drastic oxidation change is happening to some of the aromatic structures. Although there are small changes in the FTIR spectra in the area at < 870 cm^{-1} that indicate some degradation changes, the differences are not great even after

7500 h, indicating that there are areas of the resin molecules (mostly aromatic) that are relatively stable to thermal oxidation. The differential spectrum [Fig. 11(c)] confirmed the changes mentioned above.

The center of the laminate has also not been greatly affected by aging at 170°C for 7500 h [Fig. 12(a)]. The difference spectrum [Fig. 12(b)] from the starting resin, indicates some loss of OH groups and a very sharp loss of part of the 1511-cm^{-1} (aromatic) peak, which must indicate a change in a particularly susceptible (probably defect) area of the resin molecules. The high noise level of the differential spectrum emphasizes the minor nature of the changes in the original two spectra.

Thermal aging changes at 200°C

For the composite material used in this study, the aging temperature of 200°C is just below its Tg (226°C). This high temperature, while well above
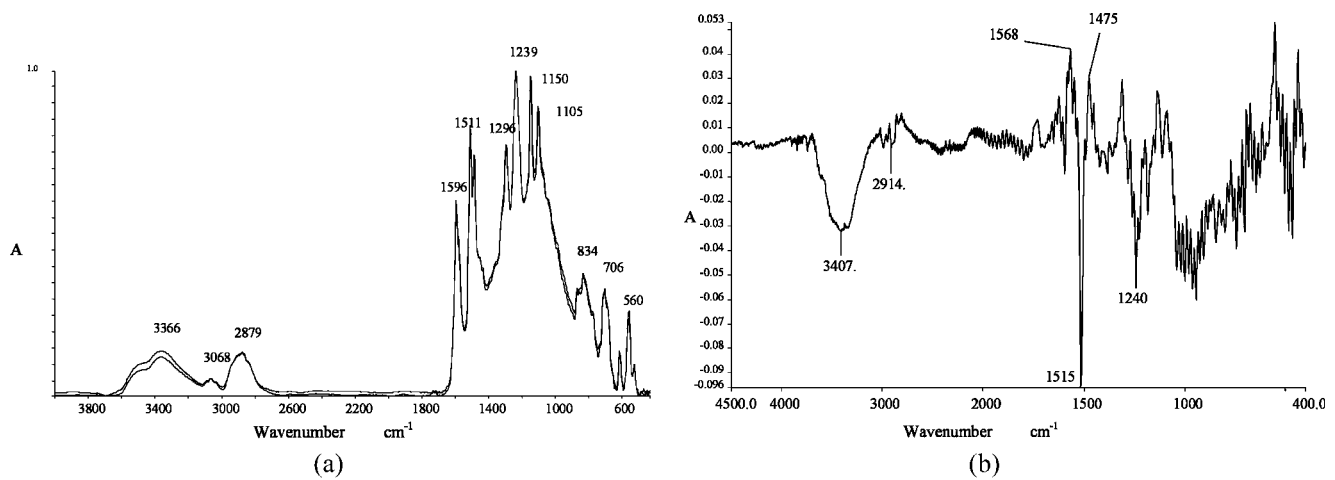
Figure 12 (a) Mid-FTIR (center analysis) spectra of 8552/IM7 aged at 170°C for 7500 h with the time zero sample. (b) Difference spectrum of un-aged 8552/IM7 and 8552/IM7 aged at 170°C for 7500 h (mid-FTIR center sample analysis).

any normal use temperature, is well within the common accelerated aging conditions used in literature degradation studies, but is known to be unacceptable for generating quantifiable accelerated aging predictions.[23,24]

It was evident quite early in the aging program that extensive general oxidation was taking place at the surface of the composite [Fig. 13(a,b)]. Many of the same types of structures were being oxidized, as shown under the 170°C aging conditions. For example, the hydroxyl and amine groups (3500–3200 cm^{-1}) decrease rapidly, as did the aromatic peaks at $\approx 1511 \ cm^{-1}$ and $1598 \ cm^{-1}$, with the former almost completely eliminated at the late stages of aging. While similar groups are being oxidized, the variety of oxidized structures being formed is much greater with at least six different carbonyl structures being

produced between 1750 and 1650 cm^{-1}. These must include ketone, carboxylic acid, and amide structures attached to aromatic and aliphatic sections, as well as the breakdown of the main polymer chains. This probably results in the total loss of material at the surface, which accounts for the greater than 3% weight drop described earlier under these conditions.

A surprising feature of the spectra is that even at the later stages of the aging program, when the aromatic structure represented by the 1511-cm^{-1} peak is completely eliminated, large areas of the molecule (as represented by peaks from 1300 cm^{-1} down) are still relatively unchanged in this particular composite. This result contrasts with our previous work with the M20/IM7 composite,[1] where the resin was completely destroyed at the surface under these con-
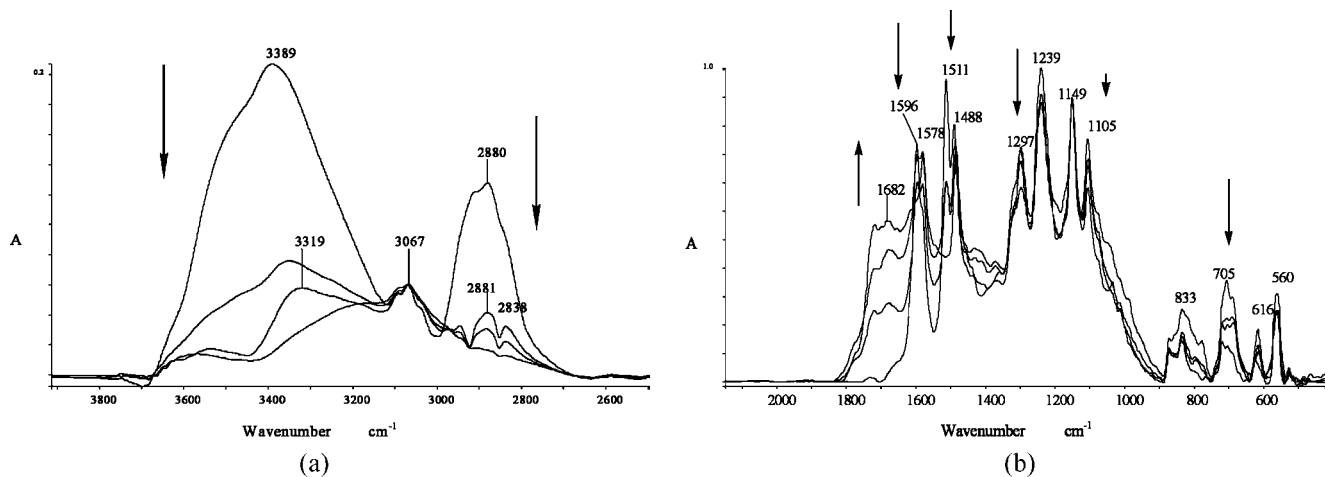
Figure 13 (a) Mid-FTIR surface spectra of 8552 IM7 aged isothermally at 200°C over 7500 h. Some of the spectral changes observed with increasing aging time from time zero to 900, 2025, and 7500 h at 200°C are shown. (b) Mid-FTIR surface spectra of 8552/IM7 aged isothermally at 200°C over 7500 h. Some of the spectral changes observed with increasing aging time from time zero to 900, 2025, and 7500 h at 200°C are shown.
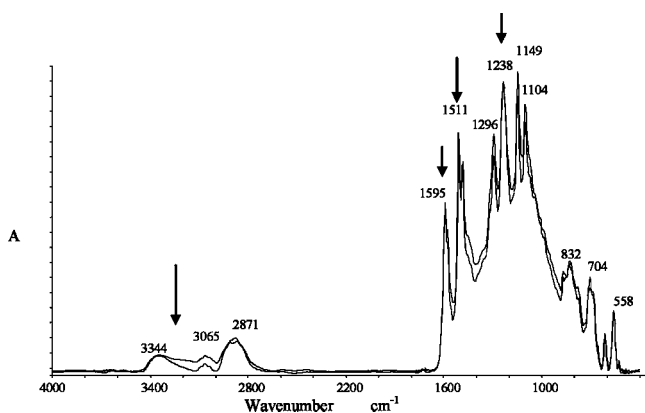
Figure 14 Mid-FTIR center spectra of 8552/IM7 at time zero and after aging at 200°C for 7500 h (and the observed changes with aging for 7500 h at 200°C).

ditions. It is likely that the immediate surface in the 8552/IM7 laminate is being oxidized away to some extent and that the areas being examined were originally under the surface and had been protected for some of the time. However, the steady progression of all the changes in the spectra, and the relatively minor changes at the lower end of the spectra, do not indicate this.

Even at the longest times and highest temperatures (7500 h at 200°C) the center of the sample was only changed slightly, with very little change due to oxidation showing (Fig. 14). The main changes observed were the decreases in OH peaks (≈ 3500 cm^{-1}) and the aromatic peaks at 1596, 1511, and 1238 cm^{-1}, but differential spectra were needed to emphasize these changes.

DISCUSSION

The analysis results have confirmed what most previous work on the thermo-oxidative degradation of epoxy resins and composites have shown, that degradation is a surface chemistry problem of the matrix resin.[6,10,25] This surface chemistry then leads to molecular stiffening, shrinking and micro-cracking, and has been detailed by a number of previous workers.[26,27] However, unlike the simple chemical changes proposed in previous studies of model epoxy systems,[14–16] the current study on the chemical degradation of a commercial epoxy/carbon fiber composite indicates that the degradation pathways are very complex and temperature and humidity dependent. Hence the modeling of real life degradation by thermally accelerated aging and Arrhenius extrapolations of the results are unlikely to produce very accurate predictions. It has been suggested by Tsotsis et al.[6] that more realistic accelerated aging

results are obtained by the use of high-pressure air aging at lower temperatures.

It appears to us that a more useful approach is to view the matrix structure as a series of very different individual groups, some of which are much more susceptible to degradation than others. For instance, at the relatively low "in service" temperatures encountered by most composite parts (usually up to $\approx 80°C$), the degradation problem may be dominated by a relatively few "susceptible defect groups" and the mechanical properties of even the surface matrix material may not be greatly affected. Above this temperature, up to $\sim 130°C$, the susceptible groups could be specific aliphatic groups in the expected epoxy-resin structure with mainly oxidative addition reactions that could stiffen the matrix molecules. Above this temperature again (up to $\approx 180°C$) the changes would include the oxidation of a much broader group of aliphatic units including those in the main chain and hence lead to surface embrittlement. Aging above 180°C would include oxidative attack in many different areas of the molecule leading to main chain breakdown and wholesale loss of surface resin material.

In applying the above generalizations to the chemical changes seen in the 8552/IM7 composite, the following degradation mechanisms can be formulated under the different aging conditions. At 70°C, the major degradation would be in the various monomer-derived defect groups such as those suggested by St John et al.,[12] where there are many methylene groups that are very susceptible to oxidation. For example, Figure 15(a) shows seven-membered rings or chloromethyl defect structures in the TGDDM monomer or glycol units from hydrolyzed epoxy ends [Fig. 15(b)].

Both weight increase and weight decrease oxidations can occur. The resulting carbonyl compounds have infrared peaks in the 1725-cm^{-1} area, but these structures are still activated for further oxidation and hence later loss. Another common monomer defect that is easily oxidized to similar carbonyl structures is the glycol group [Fig. 15(b)], which is also formed from widowed epoxy structures reacting with moisture.

At 120°C the dominating chemical change appears to be the formation of a sharp amide structure (FTIR peak at 1668 cm^{-1}) indicating the oxidation of a particular type of methylene group next to a nitrogen atom, as described by Verdu et al.[14,15] and others for neat resin aging studies. This coincides with a considerable loss in —CH$_2$ peaks in the infrared spectrum. The previously reported model compound work[9] appears to narrow this down further to the changes in the aromatic peaks (at 1597 and 1511 cm^{-1}) of mainly the TGDDM residues as shown in Figure 16.
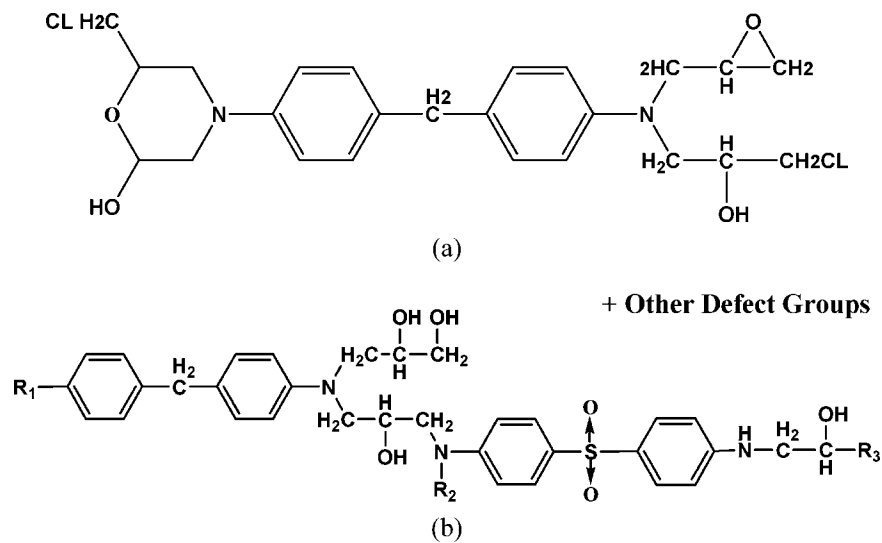
Figure 15 (a) Chloromethyl defect structures in the TGDDM monomer. (b) Glycol units from hydrolyzed epoxy ends.

The other significant chemical change at 120°C will be the oxidation of the many different secondary hydroxy groups to ketone structures with the formation of carbonyl peaks in the 1730–1710-cm^{-1} region. All these oxidation reactions will stiffen the molecular chains and lead to surface embrittlement but not great material loss (except for small quantities of uncrosslinked material) under simple isothermal aging.

At 170°C the chemistry of thermal oxidation is much more general with great loss of OH, NH and aliphatic CH and CH$_2$ peaks to give a variety of ketone, acid, and amide peaks. Even the first recorded spectrum at 400 h confirms this variety of oxidation reactions occurring, unlike the 120°C changes. By the end of the 7500 h, the aromatic region of the spectrum indicates that almost all the aliphatic —CH$_2$ groups next to the aromatic nitrogens have been oxidized, by the loss of the 1511-cm^{-1} peak. This is a peak often used as a constant for calibration in the literature aging studies of neat epoxy resins.[10,16] The weight loss results also show considerable loss of material at the surface of the composite which emphasizes that the chemical degradation mechanisms will be very varied at this temperature but only near the surface.
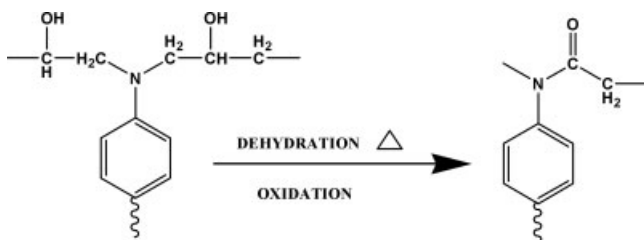

Figure 16 TGDDM residues.

Finally at 200°C the chemical mechanisms of degradation are very diverse with a very broad carbonyl region formation in the 1750–1650-cm^{-1} region showing a large increase in complete oxidation to acid groups and therefore break up of the polymer chains. While there is a very significant general broadening of the spectra between 1800 and 1000 cm^{-1}, even after 1 year the spectra from the surface has most of the same peaks and is readily recognizable. However, this may just indicate a total loss of oxidized material and a shorter oxidation time for the newly exposed material. The infrared spectrum, and hence the chemistry of the composite interior, has not been greatly affected and so the mechanical properties may show little change when carried out by some of the standard testing techniques.

CONCLUSIONS

The experimental results from these simple isothermal aging studies of the 8552/IM7 composite have indicated that the chemical mechanisms of aging can be very complex and vary greatly with the temperature of aging over the range from 70°C, which can be seen in service to 200°C which is often a temperature used in accelerated aging studies. At low temperatures ($\approx$ 70°C) the chemistry would be dominated by simple defect degradation with little influence on physical properties of a properly cured composite. At intermediate temperatures ($\approx$ 120°C), specific functional groups in the molecule are oxidized,[9] and at higher temperatures ($\approx$ 170°C) the oxidation becomes more diverse with reactions at different aliphatic sites and the formation of a range of amide and acidic groups. At high temperatures ($\approx$ 200°C), for even quite short times, the degradation

becomes catastrophic at the surface. The underlying matrix material, however, can be protected by carbon layers for a considerably longer time. Even at quite high temperatures, the degradation process takes time to affect the chemistry at the center of a thick composite part.

As a result of these (well-known) surface and edge effects[5–7] of oxidative degradation, the mechanical changes, often measured in accelerated aging tests, can lead to very errant predictions, depending on the type of test used. For example, double cantilever bend (DCB) testing measures the strength of the center of the sample.

The results reported in this work have detailed oxidative degradation caused by isothermal aging alone. ''In service'' aging can include moisture and active chemical effects, as well as thermal spiking. Some of these effects will be detailed in a later work.

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